PREPARATION OF 2-NAPHTHALDEHYDE

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IN THE course of the preparation of 2-substituted naphthalene compounds for use as plant regulators, an improved method for the synthesis of 2-naphthaldehyde was developed. It was found that N-bromosuccinimide bromination of the relatively inexpensive 2-methylnaphthalene (*1*), by a procedure analogous to that described for 1-methylnaphthalene (*2*), followed by condensation of the crude bromide with hexamethylenetetramine, according to a modified Sommlet procedure (*3*, *4*) afforded the desired product in a 64 per cent over-all yield. This method offers a number of advantages over those previously described (*4–8*).

The procedure follows.

To a solution of 71.0 g. (0.5 mol) of 2-methylnaphthalene (technical grade) in 450 g. of carbon tetrachloride (analytical grade), in a one-liter two-neck round-bottomed flask fitted with a mechanical stirrer and reflux condenser, was added 89.0 g. (0.5 mol) N-bromosuccinimide, and the reaction mixture was stirred and refluxed for 16 hours. The succinimide was filtered off, and the solvent removed under reduced pressure. The resulting brown oil was dissolved in 300 ml. of purified chloroform and added to a rapidly stirred solution of 84.0 g. (0.5 mol) hexamethylenetetramine in 150 ml. of purified chloroform in a two-liter three-neck round-bottomed flask fitted with a dropping funnel, reflux condenser, and glass paddle stirrer, at such a rate as to maintain vigorous refluxing. A white salt-like material settled out almost immediately. The mixture was heated to reflux for 30 minutes, cooled, and filtered. The crystalline hexammonium bromide product was washed with two 100-ml. portions of cold petroleum ether and then dried. Yield, 146.5 g. (79 per cent); m. p., 174–6 °C.; calculated Br, 22.12; found, 22.30.

The hexammonium bromide product was refluxed for two hours in 750 ml. of 50 per cent acetic acid solution; then 150 ml. of concentrated hydrochloric acid was added, and the solution was refluxed for five minutes more, then cooled. The aldehyde was extracted from the solution with ether, and recrystallized from a minimum volume of hot *n*-hexane. White crystalline 2-naphthaldehyde, m. p. 58.5-59.5 °C (hot stage) was obtained in a 77–80 per cent yield from the hexammonium bromide product, or a 64 per cent over-all yield from 2-methylnaphthalene. Analysis calculated for $C_{11}H_8O$: C, 84.6 per cent; H, 5.16 per cent; found: C, 84.56 per cent; H, 5.17 per cent.

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